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**THE PHENOMENON OF HOT-SALT
STRESS-CORROSION CRACKING
OF TITANIUM ALLOYS**

by W. K. Boyd and F. W. Fink

Prepared under Contract No. NASr-100(04) by
BATTELLE MEMORIAL INSTITUTE
Columbus, Ohio

for

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CRACKING OF TITANIUM ALLOYS

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INTRODUCTION

Many diverse problems require solution in order to develop a supersonic transport (SST) with the desired characteristics of maximum range and useful payload. Of primary importance is the selection of materials for the air frame and skin. Very few materials can meet the severe requirements for SST service. For example, at Mach 3 portions of the frame and skin may reach 550 F or possibly higher. Aluminum loses strength rapidly at considerably lower temperatures, so that candidate metals are limited to titanium alloys, high-strength steels, and super alloys. Of these metals, only titanium alloys possess a favorable strength-to-weight ratio, making them prime candidates for the air frame.

In addition, titanium alloys evince excellent corrosion resistance to a wide variety of environments. For example, it is well established that tensile-stressed titanium alloys at ambient temperatures are completely immune to stress-corrosion cracking in marine and other chloride containing atmospheres which may cause rapid failure of aluminum alloys, stainless steels, and high-strength, low-alloy steels. On the other hand, titanium alloys have been observed to crack in the laboratory at temperatures of 600 F or higher when the surface under tension is contaminated with dry salt. This type of failure, which has been identified as a form of stress-corrosion cracking, also has been observed during the fabrication of salt-contaminated titanium alloys at temperatures up to 1300 F.

Although titanium alloys possess a number of properties which make them very attractive for the U. S. version of the supersonic transport (SST), some concern has been expressed that the laboratory

phenomenon of hot-salt cracking may be a limiting factor in the utility of this metal in the SST. In view of this, Battelle was requested to survey the problem and prepare a state-of-the-art report.

This report presents an impartial critical review of present information to support and define wherever possible the limitations of titanium with regard to the phenomenon of hot-salt stress-corrosion cracking. The report includes:

- (1) A discussion of the factors and current state of knowledge of stress-corrosion cracking of titanium alloys by hot salt, and the mechanism of attack as presently envisioned in relation to the service conditions anticipated for the SST.
- (2) A discussion of the various laboratory procedures now being used for the evaluation of susceptibility. Comments are also made on whether or not a standardized procedure suggests itself at this time.
- (3) Identification is made of some of the gaps in the present state of knowledge on the hot-salt problem and recommendations are made for research programs to fill in these gaps.

STRESS-CORROSION CRACKING OF TITANIUM ALLOYS

Commercially pure titanium has not been found to fail by stress-corrosion cracking. Nor do the common test solutions, such as chlorides and caustics, which rapidly crack aluminum, stainless steels, carbon steels, and other common materials of construction, have any effect on titanium alloys. However, titanium alloys will stress-corrosion crack at ambient temperatures under certain specific conditions. Cracking has been encountered in red fuming nitric acid and in hydrochloric acid. Further study shows that only if the right combination of stress, metallurgical history, and environmental factors is present will cracks initiate and propagate.

Perhaps of greater interest to the present discussion is the stress-corrosion cracking associated with the vapor degreasing of titanium alloys. There is evidence that the residue from chlorinated hydrocarbon solvents contains hydrochloric acid. When susceptible titanium alloy parts are degreased in a solvent such as trichloroethylene, then heated and subjected to tensile stresses, cracks may develop leading to failure of the parts. This phenomenon has been observed in fabrication and proof-testing operations.

There may be a relationship between the stress cracking of hot titanium caused by chloride residue from chlorinated solvents and the cracking experienced in the presence of salt.

History of Hot-Salt Cracking of Titanium Alloys

Although the presence of salt as a factor was not recognized at first, the loss of properties that result when the surface is contaminated was observed in samples of titanium alloy undergoing creep testing. G. W. Bower, late in 1955, reported surface cracking of the Ti-6Al-4V alloy during creep exposure at 700 F and at about 50,000 to 60,000 psi stress. The cracking at that time was attributed to surface embrittlement induced by oxidation. Among others, TMCA and Rem-Cru Laboratories could at first not repeat the failure. Later, TMCA reported encountering the same phenomenon

on the testing of a Ti-Al-Mo-V experimental alloy at high stress and at 850 F. Duplicate tests did not give the same results. A close examination of the fractures of the embrittled specimens revealed local attack originating at the surface. These sites apparently cracked during the exposure at elevated temperature and high stress. In certain instances the cracks were associated with a mottled gray surface oxide in the pattern of fingerprints. It was suggested that some ingredient in human perspiration might be associated with the cracking. Testing of specimens in contact with pure sodium chloride produced cracking. Cracking was apparent later as a result of a type of stress corrosion involving elevated temperatures, high stress, and sodium chloride. Investigators at Pratt and Whitney, ITT Research Foundation, the titanium producers' laboratories, Battelle, etc., confirmed these results independently.

At about this same time, cracking was observed on some hot-formed sheet materials. These cracks appeared to be associated with the use of temperature-indicating compounds. Later these compounds were found to contain chloride salts. The use of chloride-free marking materials greatly reduced cracking.

In those early days the Pratt and Whitney Aircraft Laboratory studied in detail the factors in the stress-corrosion cracking of titanium. Their early summary is published in TML Report 88 of the Titanium Metallurgical Laboratory (now called Defense Metals Information Center at Battelle). Pratt and Whitney subjected heavily salted discs and blade assemblies of the J-57 engine to elevated-temperature bend tests, using various air flow velocities. These tests approached the type of compressor salt exposures anticipated in service operation. Temperature and stress levels, however, were above those used in current production engines. Titanium discs in Pratt and Whitney engines in service are designed to operate at a maximum temperature of 750 F. The maximum diametrical growth in creep is limited to 1/10 of 1 per cent. High-velocity aircraft experience on discs has indicated that the stresses which produce creep extensions up to 1/10 of 1 per cent at temperatures up to 800 F do not cause stress-corrosion cracking in the presence of salt in service.

Early workers recognized that since temperatures as high as 600 F are possible on the leading edges of the exposed titanium structural members of the Mach 3 supersonic transport, the problem of hot-salt stress-corrosion cracking would be important.

Fabrication Experience

Convair has studied the problem of susceptibility to stress-corrosion cracking during shop processing. A comparison was made of Ti-7Al-12Cr and Ti-5Al-5Zr-5Sn with Ti-8Al-1Mo-1V.

Tests were conducted at 1300 F since this temperature was selected as typical of what may be required in a hot forming or a hot sizing operation. Distilled water containing either 100, 200, 400, 600, or 1000 parts sodium chloride was applied to the titanium surface. Samples were stressed by bending specimens 0.032 x 1 in. x 12 in into a hoop having a 2-1/2 in. radius and restrained in this position with stainless steel wire. Exposure times were 1/2 hour at 1300 F.

All three alloys were found susceptible to hot cracking from intergranular corrosion caused by salt deposits or by the residues from the experimental rinse waters containing as little as 100 ppm NaCl. Salt concentrations of the order of 400 ppm are found in the tap water available in San Diego.

All three alloys in the program were found to be susceptible to hot-salt stress-corrosion cracking during shop forming. Convair maintains constant vigilance in order to be certain that parts are free of chlorides before any heating operations such as hot forming, hot sizing, stress relieving, or welded assembly. For example, all parts are hand cleaned after chemical etching and then handled with white gloves. All tools for hot sizing are steam cleaned to remove forming lubricants and sand blasted and cleaned with alcohol and coated with molybdenum disulfide lubricant. By purposely avoiding all salt during fabrication no trouble has been experienced.

The Ti-8Al-1Mo-1V alloy is found to be very susceptible to hot-salt cracking under the conditions encountered in fabrication shops. The only factor in this situation that can be eliminated and still make assembled aircraft structures is the salt.

In both Pratt and Whitney shops and in their subcontractor shops a continuous survey is made to eliminate procedures involving the danger of surface embrittlement through interstitial absorption. Salt is not the only source of cracking. Early experience in fabricating titanium shows that brittle surface layers were produced when the material was heated in air at elevated temperatures. This oxygen enrichment produces multiple surface cracking when the material is deformed as in bending.

The bend tests were found to be the most rapid and economical means for detecting this adverse condition. The maximum exposure time for heating titanium in air ranges from seconds to hours depending on whether the temperature is up in the range of 1600 F or down as low as 1000 F. There is a definite difference in alloys and their susceptibility to surface embrittlement through interstitial absorption.

Jet Engine Experience

Pratt and Whitney Aircraft has had more and earlier experience with titanium than any other firm. In 1952 they tested their first titanium compressor rotor and in 1954 the first J-57 engine containing titanium components was put into service. For several years the J-57 engine program consumed over 50 per cent of the United States production of titanium. Several thousand J-57 engines containing 10 to 15 per cent titanium have served in a variety of aircraft. The more recent and more powerful Pratt and Whitney J-75 engine has accumulated more than six million hours of flight time in commercial and military aircraft. Table 1, which is extracted from the Pratt and Whitney report, shows the large percentage of titanium used in the jet engine and the long periods between overhaul (up to 4000 hours).

TABLE 1. WEIGHTS OF TITANIUM COMPONENTS OF TYPICAL
PWA GAS TURBINE ENGINES USED IN VARIOUS
MILITARY AND COMMERCIAL AIRCRAFT

Engine	Weight of Titanium, lb	Titanium Portion of Total Engine Weight, per cent	Aircraft	Time Between Overhauls, Hours	Operator
JT3D-1	565	13.8	Boeing 707 Boeing 720 Douglas DC8	2600 2600 2200	Pan American Airways Pan American Airways United Air Lines
TF33P-5	565	13.4	Boeing C-135B	2400	MATS, USAF
TF33P-7	637	13.9	Lockheed C-141	2400 (1)	MATS, USAF
J57P-43W	586	15.6	Boeing B-52	(2)	SAC, USAF
JT4A-5	385	8.1	Boeing 707 Douglas DC8 Douglas DC8	4000 4000 4000	Pan American Airways Pan American Airways Eastern Air Lines
J75P-19W	677	11.6	Republic F-105	600 (1)	TAC, USAF
JT8D-1	351	11.6	Boeing 727	(2000 basic) (3)	Various

- (1) Maximum hours of operation before removal of engines as specified in USAF T.O. 2-1-13.
- (2) A specified maximum operating time has been eliminated for these engines. Engines will be removed for major overhaul based on condition of engine and extent of maintenance possible at field level.
- (3) Initially, sample engines will be overhauled at 1200 hours, 1500 hours, and 1800 hours.

Pratt and Whitney chose titanium alloys for the fan and compressor blading to take full advantage of corrosion and oxidation resistance, low density, high fatigue strength, high creep strength, and an extremely tough ductile metal structure. The highest compressor service temperature that they have reached with titanium alloys thus far is about 750 F. Experience has borne out the decision to use titanium alloys. Pratt and Whitney have experienced no hot salt fatigue or hot-salt stress-corrosion cracking failures in service on any of their titanium alloy compressors or other titanium parts of the jet engines. Stresses on these titanium components, on the other hand, are believed to be lower than would be used in structural design. However, considering the long time in service, and the temperature range involved, it would be expected that some failures would have been reported by this time if there were a problem in this type of service.

Based on their laboratory experience with Ti-8Al-1Mo-1V alloy they believe this material could be used with safety at 500 or 550 F.

Compressor discs designed for service above 500 F usually are limited by creep strength. A typical criterion is the stress required to produce 1/10 of 1 per cent plastic deformation at 150 hours. Now that the range of temperature in the compressor is being extended, the creep properties of the Ti-6Al-4V alloy are being compared with the higher strength Ti-8Al-1Mo-1V and Ti-5Al-5Zr-5Sn alloys. Information is needed on the relative order of resistance of these three alloys to hot-salt stress-corrosion cracking.

General Electric also has had years of experience in the jet engine development program. An engine identified as the J79-8 is supplied for the McDonnell Aircraft F-4B. This is a two-engine supersonic plane. The Ti-6Al-4V alloy is used in the compressor section for the wheels. The blades are made of Type 403 stainless steel. There are 17 stages. In Stages 1 through 7 the maximum temperature of 570 F is expected. This aircraft sees extensive service on the decks of, and in flight over, aircraft carriers for the Navy.

General Electric also uses an alloy referred to as B5F5, which is a modified 4350 chrome-molybdenum-vanadium alloy steel. Minor corrosion

pitting has been observed on the wheels or discs made of this alloy. This is attributed to the marine salt picked up in service. The maximum temperature reached on steels is 1050 F at a peak stress of 70,000 psi. The stress levels on the blades are low, probably less than 20,000 psi.

At some of the sites in the compressor the air circulation is negligible. In other words, the environmental condition is not too different, apparently, from a sample in a creep furnace. In spite of this, there have been no failures in service of any kind, according to discussions at General Electric.

In another engine, the J93, Ti-7Al-4Mo alloy is used for blades, vanes, discs, and rings in the compressor. Ti-5Al-2.5Sn also is used for some components. Temperatures range from 500 to 600 F and stress levels can be 80,000 to 85,000 psi or very close to the yield. The maximum temperature for 3.2 Mach operation would be 900 F with peaks as high as 1015 F.

There are no special handling precautions in assembling the titanium compressor for the J93. Purple tints showing oxidation are found after exposure. Often fingermarks are outlined by the oxidation pattern. The vane received hot compressor air for anti-icing control at roughly 900 F. The velocity is of the order of 1000 feet per second. No failures have been reported up to the present for this alloy under these severe conditions.

It should be pointed out, however, that the J93 has been operated only at G.E.'s Evandale, Ohio plant and at Palmdale, California, although some salt could be contained in the desert soil.

Airframe Experience

Some titanium is incorporated into the airframe of most of today's high performance aircraft used by the military. As far as can be ascertained, none of these parts has ever failed because of hot-salt stress-corrosion cracking. On the other hand, the indications are that with the possible exception of the new A-11 (built by Lockheed), these titanium components are not subjected during flight to the critical combination of

stress and temperature known to initiate cracking in the laboratory. For example, it is believed that few, if any, of the titanium airframe components are subjected to temperatures above about 425 F. Furthermore, operating stress levels of such parts are quite low, about 15,000 to 20,000 psi maximum. In addition, exposure times at maximum temperatures and stress levels are of short duration.

On the basis of the information available it would appear that performance data for titanium components in existing airframes may not be directly applicable to the SST. However, the fact that no hot-salt failures have been reported is encouraging. It is also expected that performance of titanium in the A-11 airframe will be more closely related to that anticipated for the SST.

Laboratory Creep Testing

Most of the experimental data on the hot salt stress-corrosion cracking problem has been developed using creep testing facilities. For studying such variables as time, temperature, and stress, creep testing facilities can be readily adapted to the problem. In some laboratories other variables have been introduced, such as the effect of (a) cyclic exposures, (b) variations in the composition of the salt and methods of applying it, (c) metallurgy of the titanium alloy, and (d) coatings to mitigate the attack.

Information was made available from Douglas Aircraft giving the results of a titanium alloy stress-corrosion study which was subcontracted to investigators at McDonnell Aircraft. A final report is about to be issued. This experimental work made use of creep furnaces which were run at temperatures somewhat higher (600, 700, 800 F) than the range of major interest to the SST structural program (400 - 550 F). While it is difficult to predict 36,000-hour life in service from the 100-hour data developed in the McDonnell Laboratory, a few interesting results can be mentioned.

Douglas and McDonnell, under their test conditions, established that titanium alloy samples first exposed to sea air on the El Segundo

Beach were just as susceptible to hot-salt cracking in a creep furnace as samples that were coated with synthetic sea salt in the laboratory.

In the temperature range of 600, 700, and 800 F, it can be concluded from the stress-corrosion test results that the Ti-6Al-4V alloy under tensile stress rapidly loses its load-carrying ability as a result of the salt application as compared with the corresponding creep strength for uncontaminated samples. Similar loss of properties is found for Ti-8Al-1Mo-1V, Ti-4Al-3Mo-1V, Ti-5Al-2.5Sn, and 5Al-1.25Fe-2.75Cr (RS140) alloys.

One aspect of the problem of hot-salt stress-corrosion cracking is the difficulty of establishing when the test specimen has, for all practical purposes, lost its load-carrying ability.

A technique developed at Langley Field has led to considerable information for the Ti-8Al-1Mo-1V and for three other structural alloys. A specially designed bend sample is employed. At frequent time intervals a few salted and stressed samples are removed from the creep furnace and checked for damage. Thus, a continuous record is available of the deterioration of the given alloy.

By making use of large numbers of specimens and carrying out the tests for long periods of the order of 3000 to 8000 hours, results of value to the SST program have been obtained.

A summary of their data is given in Figure 1. Note that the Ti-4Al-3Mo-1V alloy at 100 ksi and the Ti-6Al-4V alloy at 50 ksi showed no loss of strength for the entire period on test. The Langley Field results clearly demonstrate differences in the susceptibility of various alloys to stress-corrosion cracking by hot salt.

Work in progress at North American Aviation, Los Angeles, is developing long-time results for titanium alloys. Dead weight cantilever-type samples are being exposed at 650 F. One set of salt-coated samples is continuously exposed at temperature in the circulating air furnace, another set is given a cycle in which the samples are exposed alternately to two weeks in the furnace at temperature, and then to two weeks in a tropical humidity chamber at 100 F.

For a time interval of 13,240 hours and for the conditions of (a) no salt, (b) salt coated, and (c) salt plus cycle, the following

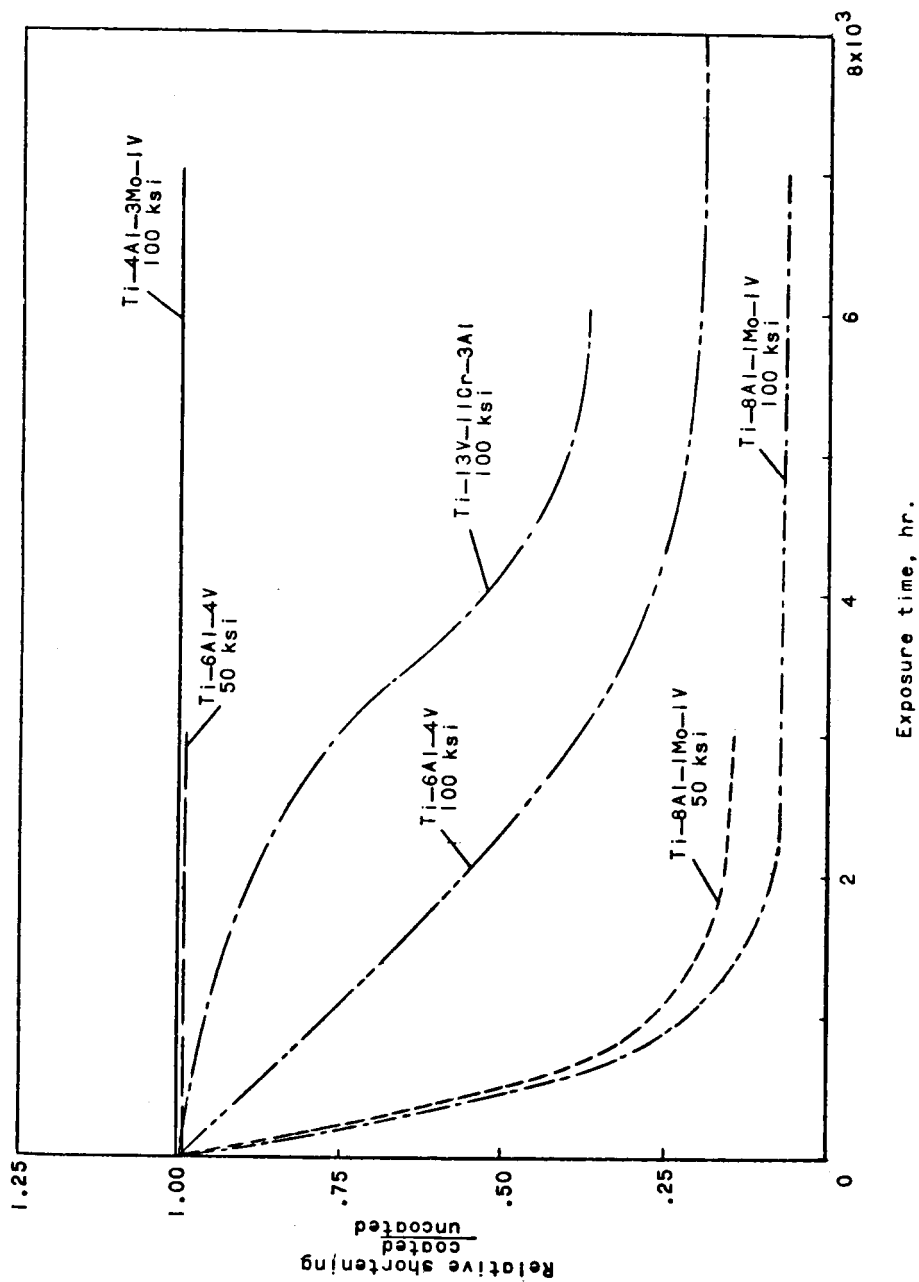


FIGURE 1. RELATIVE SHORTENING OF COATED SPECIMENS
AS A FUNCTION OF EXPOSURE TIME

results were obtained.

Alloy	NAA Test Results at 13,240 hours at 650 F		
	No Salt*	Salt*	Salt Plus Cycle**
Ti-6Al-4V	No Failure	No Failure	No Failure
Ti-8Al-1Mo-1V	No Failure	2 Failures	No Failure

* 5 samples

** 4 samples

It is important to note that the time at temperature for the samples being cyclically exposed is only half that for the samples held continuously at temperature. This may be a factor in explaining why none of the four samples in each set in the salt-plus-cycle condition has failed. These tests are being continued.

In considering the fact that a study of stress-corrosion cracking of titanium alloys must be made on the basis of a statistical approach, it would be desirable to greatly increase the number of samples undergoing cantilever salt testing at NAA. Variations in exposure, such as the use of a cycle, are very important. It may be that the time in the humidity cabinet could be reduced to one day, thus allowing more time at temperature. The use of higher stresses at lower temperature also would be of interest to the SST program.

Other Laboratory Investigations

At Renton, Washington, Boeing Aircraft has an interesting experimental arrangement for the study of stress-corrosion cracking. The sample is exposed to a cycle which consists of immersion in 3-1/2 per cent salt solution, heating to 550 F and then air cooled.

The choice of 550 F for the high-temperature portion of the exposure and the provision of a cycle make this experimental arrangement of considerable interest to the SST program. It is understood that Boeing's "in-house" program will be expanded to allow for the study of a number of variables.

Some preliminary results for Ti-8Al-1Mo-1V were provided by Boeing showing (a) exposure to 40 ksi at 500, 550, and 600 F for 1000 hours, and (b) cyclic exposure at 87 ksi for 1000 hours. This latter cycle was as follows:

15 min	70 - 550 F
35 min	550 F
10 min	550 - 70 F

A 3.5% NaCl solution is used to immerse the sample at room temperature. Stresses are set at 50, 75, and 90 per cent of yield. The Ti-8Al-1Mo-1V alloy is being used with the duplex annealing treatment.

At 40 ksi and a temperature of 500 F no failure was observed at 2625 hours, as shown in Table 2. At 550 F one sample failed in less than 1000 hours and the other showed serious loss of properties at 1000 hours.

Research on the Mechanism

Materials Research Laboratory has been studying the fundamental mechanism of the salt stress corrosion of Ti-6Al-4V. Their apparatus makes it possible to provide a controlled atmosphere next to the Ti-6Al-4V anode, which is the couple member under stress. At the cathode, air at normal pressure is provided. A dry-salt bridge completes the electrochemical circuit between the two electrodes. They propose to observe crack length for different controlled pressures at the anode up to atmospheric. Cell current also will be measured. By this procedure they plan to obtain evidence on the fundamental species which follow grain boundaries under

TABLE 2. Ti-8Al-1Mo-1V^(a) CORROSION TESTING SALT SLURRY
AND CONSTANT STRESS (40,000 psi)

	F _{tu}	F _{ty}	Elongation, per cent in 2"
T = 500 F; t = 1000 hr	152.6	139.2	12.5
	153.5	138.2	13.5
T = 500 F; t = 2625 hr	154.5	138.2	13.0
	155.0	138.7	12.5
T = 550 F; t = 1000 hr ^(b)	113.0	90.8	10.0
		--	
T = 600 F; t = 1000 hr	56.1	--	0.4
	66.7	--	0.5
Pre-exposure data	143.0	132.0	14.0

(a) All material from Heat No. D3457 TMCA.

(b) One specimen failed in less than 1000 hr.

TABLE 3. Ti-8Al-1Mo-1V DUPLEX ANNEAL 3.5% NaCl SOLUTION
CYCLIC TEMPERATURE (1000 hours at 87 ksi)

	F _{tu}	F _{ty}	Elongation in 2"
Pre-exposure	143.0	132.0	14%
Post-exposure	154.0	138.4	12%

The program in progress at Boeing is employing the following cycle:

10 min	Room to 550 F
150 min	550 F
10 min	550 F to room temperature
10 min	at room temperature

stress. If the attack is caused by chloride ions in a relatively non-volatile compound, air pressure should have little effect. On the other hand, if a volatile chloride is involved, the reaction should be sensitive to the ambient pressure at the anode.

DISCUSSION OF THE PHENOMENON AND MECHANISMS OF HOT-SALT STRESS-CORROSION CRACKING OF TITANIUM ALLOYS

Nature of Attack

The examples of hot-salt cracking of titanium discussed in published reports or during visits to the various laboratories engaged in researching the problem show the attack to be predominantly intergranular in nature. This is not surprising, since the chemical activity of the titanium alloy grain boundary should be affected by boundary disorder and the disordering effects of stress and deformation. In addition, if there is segregation or absorption of solute atoms or interstitials at grain boundaries this also would affect grain boundary activity. For many alloy systems selective attack of grain boundaries can be initiated in a given environment in the absence of applied and/or residual tensile stresses.

Consideration of Other Alloy Systems Exhibiting Intergranular Cracking

It is of interest to consider the environment-alloy combinations that lead to intergranular failure of tensile-stressed samples. One of the oldest to be identified is the season cracking of brass in ammoniacal atmospheres. Pure copper is immune to cracking under similar conditions.

Aluminum alloys suffer intergranular stress-corrosion cracking in chloride solutions. In this case it has been found that the cracking occurs as the result of the formation of intermetallic compounds, or zones around the compounds, which are highly anodic to the body of the surrounding grains.

Under specific conditions caustics will cause intergranular cracking of nickel-base alloys, carbon steel, and copper-base alloys. Some low alloy and carbon steels also exhibit intergranular failures in nitrate and chloride solutions.

Intergranular embrittlement of aluminum-, titanium-, gallium-, iron-, and copper-base alloy systems by mercury, cadmium, zinc, gallium, and other low-melting-point metals is well documented. In each case cracking occurs in the presence of tensile stress only if the embrittling agent is in the molten form.

It has been found that NaCl and other halide salts will cause intergranular attack and/or cracking of austenitic stainless steels and some nickel- and cobalt-base super alloys. In the case of the stainless steels, stress is not found to be a factor, and the mechanism of the attack is believed that of accelerated preferential oxidation of grain-boundary carbides. Attack of the super alloys only occurs at high temperatures well above the melting point of NaCl.

In each of the alloy systems previously discussed, stress-corrosion cracking occurs only in the presence of a liquid or gas. No instance of stress-corrosion cracking has ever been recognized as such when the environment was completely solid.

From these facts and experiences it is logical to expect that a liquid or gas phase needs to be present in order to account for the hot-salt cracking of titanium alloys. In the study of possible reactions an effort has been made to find chemical reactions which could lead to a liquid phase at temperatures of the order of 550 F or higher and a solid phase below this temperature.

Thermodynamic Considerations*

Thermodynamic considerations were used to postulate chemical reactions which may be involved in the hot-salt stress-corrosion cracking

* Dr. James J. Ward of the Battelle staff assisted the authors in developing the concepts presented here.

of titanium alloys. In this work it is realized that thermodynamics gives no information on the rate of corrosion or on the path followed in the actual corrosion reaction. The value of the thermodynamic approach is that any postulated corrosion mechanism must have initial and final states as well as intermediate steps that are in agreement with thermodynamic principles. In the preparation of this section, the work of Crucible Steel, ITT Research Institute, and others was reviewed.

Basic data for the thermodynamic considerations are given in Table 4. From the data in Table 4, the standard free energy of reactions of interest were calculated and are given in Table 5. These reactions are helpful in speculating on corrosion mechanism and on the various stages in the observed attack.

Reaction 1 in Table 5 gives the primary corrosion reaction. The reaction product Na_2O can in turn react with water vapor to form molten NaOH as listed in Reaction 11. Reactions 2 and 3 also show the possibility of forming liquid sodium. The molten NaOH could be expected to dissolve NaCl and possibly TiCl_2 to give a liquid system at temperatures even lower than about 600 F. It can be envisioned that chloride ions could be transported by the molten NaOH thus allowing the corrosion within crevices by this mechanism to continue. Molten caustic itself is very corrosive to titanium whether chlorides are present or not. If the caustic were formed only near the anode, as might be expected, it could account for attack above 600 F.

Reactions 6 and 7 of Table 5 indicate the formation of a gaseous TiOCl_2 from TiCl_2 and O_2 . This reaction would leave Na_2O as the only solid reaction product. If a gas is responsible for the intergranular attack, the attack would be expected to decrease as the air movement over the sample was increased, and there is some evidence that this may be so. On the other hand, if gaseous reaction products are necessary for cracking, then just heating a salt-titanium mixture could be expected to crack a titanium sample not in contact with the salt, but this is not the case.

Reactions 4 and 5 predict that TiCl_2 rather than a higher chloride is the thermodynamically stable chloride. The formation of TiCl_4 gas in Reaction 5 may be regarded as a disproportionation of TiCl_2 in Reaction 2.

TABLE 4. STANDARD FREE ENERGY OF FORMATION OF SOME COMPOUNDS OF INTEREST
IN STRESS-CORROSION CRACKING OF TITANIUM ALLOYS

Compound	ΔF_f° , kcal/gmole			
	Temperature			
	400 K 260 F	500 K 440 F	600 K 620 F	700 K 800 F
1.. NaCl(s) ⁽¹⁾	-89.522	-87.262	-84.998	-82.765
2. Na ₂ O(s)	-86.620	-83.098	-79.578	-76.072
3. Na ₂ O ₂ (s)	-101.800	-96.40	-91.10	-85.90
4. NaOH(s) or (l) ⁽²⁾	-86.498(s)	-83.122(s)	-79.857(1)	-76.725(1)
5. NaAlO ₂ (s)	-252.454	-247.122	-241.794	-236.481
6. Na ₂ TiO ₃ (s)	-348.480	-342.290	-334.900	-328.640
7. TiCl ₂ (s)	-108.238	-104.653	-101.125	-97.646
8. TiO ₂ (s)	-207.780	-203.399	-199.063	-194.765
9. TiCl ₃ (s)	-150.321	-145.115	-140.004	-134.979
10. TiCl ₄ (g) ⁽³⁾	-170.712(1)	-167.589(g)	-164.633	-161.750
11. TiOCl ₂ (g)	-127.015	-126.158	-125.295	-124.425
12. O ₂ (g)	0	0	0	0
13. O ₃ (g)	+40.601	+42.272	+43.940	+45.605
14. H ₂ O(g)	-53.517	-52.359	-51.155	-49.912

(1) s = solid

(2) l = liquid

(3) g = gas

TABLE 5. STANDARD FREE ENERGY CHANGE OF SOME REACTIONS
OF POSSIBLE INTEREST IN STRESS-CORROSION
CRACKING OF TITANIUM ALLOYS

Reaction	Standard Free Energy Change of Reaction, ΔF_R° ; kcal				
	Temperature				
	400 K 260 F	500 K 440 F	600 K 620 F	700 K 800 F	
1. $\text{Ti(s)}^* + 2\text{NaCl(s)} + 1/2 \text{O}_2(\text{g})^* = \text{TiCl}_2(\text{s}) + \text{Na}_2\text{O(s)}$	-15.814	-13.227	-10.707	-8.188	
2. $\text{Na}_2\text{O(s)} + 1/2 \text{Ti(s)} = 2\text{Na(l)}^* + 1/2 \text{TiO}_2(\text{s})$	-17.270	-18.602	-19.954	-21.311	
3. $3/2 \text{Ti(s)} + 2\text{NaCl(s)} + 1/2 \text{O}_2(\text{g}) = \text{TiCl}_2(\text{s}) + 1/2 \text{TiO}_2(\text{s}) + 2\text{Na(l)}$ (sum of Nos. 1 and 2)	-33.084	-31.829	-30.661	-29.499	
4. $2/3 \text{Ti(s)} + 2\text{NaCl(s)} + 1/2 \text{O}_2(\text{g}) = 2/3 \text{TiCl}_3(\text{s}) + \text{Na}_2\text{O(s)}$	-8.712	-5.221	-2.825	-0.528	
5. $1/2 \text{Ti(s)} + 2\text{NaCl(s)} + 1/2 \text{O}_2(\text{g}) = 1/2 \text{TiCl}_4(\text{g}) + \text{Na}_2\text{O(s)}$ [The disproportionation of $\text{TiCl}_2(\text{No. 1})$ to give Ti and TiCl_4 would lead to No. 5]	+7.068	+7.631	+8.101	+8.583	
6. $\text{TiCl}_2(\text{s}) + 1/3 \text{O}_2(\text{g}) = \text{TiOCl}_2(\text{g})$	-18.777	-21.505	-24.170	-26.779	
7. $\text{Ti(s)} + 2\text{NaCl(s)} + \text{O}_2(\text{g}) = \text{TiOCl}_2(\text{g}) + \text{Na}_2\text{O(s)}$ (sum of numbers 1 and 6)	-34.591	-34.732	-34.877	-34.967	
8. $\text{Ti(s)} + 2\text{NaCl(s)} + 1/3 \text{O}_3(\text{g}) = \text{TiCl}_2(\text{s}) + \text{Na}_2\text{O(s)}$ (cf. No. 1 with O_3 substituted for O_2)	-29.334	-27.304	-25.352	-23.374	
9. $2\text{NaCl(s)} + 2\text{Ti(s)} + 3/2 \text{O}_2(\text{g}) = \text{TiCl}_2(\text{s}) + \text{Na}_2\text{TiO}_3(\text{s})$	-277.674	-272.419	-266.029	-260.756	
10. $2\text{NaCl(s)} + 2\text{Ti(s)} + \text{O}_3(\text{g}) = \text{TiCl}_2(\text{s}) + \text{Na}_2\text{TiO}_3(\text{s})$	-318.275	-314.691	-309.969	-306.361	
11. $1/2 \text{Na}_2\text{O(s)} + 1/2 \text{H}_2\text{O(g)} = \text{NaOH(l)}^{**}$	-16.429(s)	-15.393(s)	-14.510(1)	-13.733(1)	
12. $\text{Na(l)} + \text{H}_2\text{O(g)} = 1/2 \text{H}_2(\text{g}) + \text{NaOH(l)}^{**} \text{ or } (\text{s})$	-32.981	-30.763	-28.702	-26.813	
13. $2\text{NaCl} + 1/3 \text{O}_3(\text{g}) = \text{Na}_2\text{O(s)} + \text{Cl}_2(\text{g})$	+92.424	+91.426	+90.418	+89.458	
14. $3\text{NaOH(l)} + \text{Al(s)} = \text{NaAlO}_2(\text{s}) + \text{Na}_2\text{O(s)} + 3/2 \text{H}_2(\text{g})$	-79.580	-80.854	-81.800	-82.380	

* s = Solid
l = Liquid
g = Gas

** 606.4 F or below.

The thermodynamic driving force of ozone instead of oxygen is shown to be very much greater in the corrosion reaction. This conclusion may be reached by comparing Reactions 8, 10, and 13 with Reactions 1 and 9. This is of interest because at 75,000 feet, the SST would be expected to cruise in a rarified air containing a higher percentage of ozone as compared with low altitudes.

Role of Oxygen

It is believed by some investigators that in order for hot-salt cracking of titanium to occur some oxygen must be present. The oxygen may be either in the gaseous form or supplied by a reducible oxide. There is considerable evidence of the need for oxygen. For example, in the case of stainless steels it has been found that the higher the concentration of oxygen in the cracking environment the lower the stress levels necessary to initiate cracking, and the shorter the time to initial cracking. These observations, however, do not necessarily indicate that cracking cannot occur in the complete absence of oxygen.

It also should be remembered that even if it can be established that titanium will not crack in the absence of oxygen the exclusion of oxygen from the surface of the SST would not be a practical solution to the problem.

Role of Water Vapor

The effect of moisture either as water of hydration in the salt or as vapor in the atmosphere has not been thoroughly investigated in relation to the occurrence of cracking. In considering the role of moisture in titanium corrosion reactions it could be predicted that moisture might play a significant role. For example, the presence of only a small amount of water has been found to inhibit stress-corrosion cracking of titanium alloys in red fuming nitric acid. In addition, dry

chlorine rapidly attacks titanium, while wet chlorine gas (2% moisture) attacks titanium only slightly. Similar effects of moisture have been observed for other metal and alloy systems.

Further evidence that water vapor may be important is found from a consideration of the environment existing in jet engines where no hot-salt cracking failures have been observed to date. In any case, the normal composition of the air results in higher humidity content.

These observations appear to suggest strongly the possibility of the existence of a critical moisture level (or relative humidity) where cracking may occur rapidly. Above or below this level cracking may be retarded or completely inhibited. The role of water warrants further research.

Role of Hydrogen

The embrittling effect of hydrogen on most of our common materials of construction, including titanium, is well documented. Although some of the reactions previously discussed can result in the liberation of hydrogen, there is no evidence to suggest that cracking is directly related to loss of ductility resulting from hydrogen pickup. However, it would be interesting to analyze hot-salt cracked samples of titanium to determine if they are high in hydrogen after exposure.

Gaseous Versus Liquid Reaction Products

Two schools of thought exist as to the mechanism of the cracking. One suggests that chlorine and/or hydrogen chloride gas is responsible for the cracking and the other postulates attack by a low melting point salt mixture based on sodium hydroxide. There is evidence to support both theories but it would appear that the data favor the need for a liquid phase.

For example, if chlorine or HCl gases were involved, cracking of non salt-coated specimens would be expected to occur if the specimens were exposed in the vapor phase above hot sodium chloride or in the same

furnace containing salt-coated specimens. Cracking does not occur under these conditions, however, and in fact it has been found that no cracking does occur unless the salt is actually in contact with the specimens. Furthermore, crack initiation appears to occur along the outer edge of the salt coating, and if the crack propagates outside the salt cover it stops until the salt again creeps to cover the cracked area.

Possibly the most important piece of evidence favoring the necessity for a liquid phase is the fact that no cracking has been observed at temperatures of 500 F and below. Most of the possible salts and corrosion products have melting points in excess of 500 F. Gases, however, would be expected to be active at temperatures below 500 F. One further bit of data favoring the liquid phase theory is the observation that lower melting point salts are the most active, and sea salt, which contains a number of elements, is more aggressive than the ASTM synthetic salt (3% NaCl + 0.5% MgCl₂), which in turn causes more rapid cracking than pure NaCl.

Electrochemical Aspects of the Problem

It is generally agreed that true cases of stress-corrosion cracking involve an electrochemical step, at least in part. The electrochemical approach to the hot-salt cracking of titanium has been given some consideration. Information developed to date is not conclusive, but does suggest that further research in this area might be fruitful. Certainly if it could be established that the mechanism of cracking is electrochemical in nature it would be further evidence for the presence of a liquid phase.

Stress

Either residual or applied tensile stresses are a necessary prerequisite for stress-corrosion cracking. In general, the higher

the stress levels the shorter the time to failure. For most systems there is a critical stress level below which no cracking is initiated. In the case of the hot-salt cracking of titanium this critical stress level has not been established and the effect of plastic and elastic deformation has not been defined. There is some indication that unless there is a small amount of plastic deformation cracking may not occur. It will be remembered that the occurrence of hot-salt cracking was first observed during creep testing. In addition, titanium does not become embrittled by liquid mercury unless it is subjected to plastic deformation while in contact with the mercury. Simply stressing the titanium and then immersing it in a bath of mercury will not cause fracture. It is also felt that the effects of plastic versus elastic deformation should be studied.

DISCUSSION AND CONCLUSIONS

There seems to be a difference of opinion among the government agencies and industrial companies who have a vital interest in the development of the SST as to whether a Mach 2.5 supersonic transport or a Mach 3.0 transport should be developed at this time. A titanium alloy would be favored for either design. However, for the 2.5 design it would not be necessary to be concerned with the hot-salt cracking problem of a titanium alloy, at least not so far as the fuselage in the leading wing edges is concerned. There may be areas on the fuselage aft of the engines where higher temperatures might be encountered as a result of the exhaust. However, these areas could be provided for by an oxidation-resistant metal not subject to salt deterioration. In any case, the problem of using a titanium alloy for a Mach 3 supersonic transport must be faced some day, if not now. Also, the earlier the research problems are outlined the better, since long-time effects need to be investigated in greater detail.

The well known TML Report No. 88, in which a group of industrial organizations working on the hot-salt problems with titanium alloys pooled their knowledge, still contains in essence the main facts known today

about the problem. Although additional information is now available, the fact remains that it has yet to be established that the hot-salt problem exists in service. Although considerable titanium is used in jet engines at temperatures known to cause hot-salt cracking, no failures have been reported. While it is true that conditions in an engine may be much different from those in an airframe, it might be expected that at some time conditions favoring cracking would be reached in engine service.

A plot of the results from various laboratories on the basis of applied tensile stress versus temperature is shown in Figure 2. The results for time versus stress in the temperature range 500 to 900 F are presented in Figures 3 through 11 inclusive. It should be noted that from the limited amount of data available failures are reported for tensile loads as low as 25 ksi at 650 F, and 40 ksi at 600 F and 550 F. There are no failures reported at 500 F and below.

If the time versus stress data for 550 F are examined, it will be observed that failures have been recorded at around 100 hours at stresses of the order of 50,000 psi. In another case failure was observed at less than 1000 hours at 40,000 psi. At lower stresses longer times are required to obtain failure or loss of properties. Raising the temperature usually shortens the time to failure. However, it has not been proved conversely that lowering the temperature to 500 C would cause titanium alloys to have a life time greater than 30,000 or 40,000 hours.

Examination of the data that are available would suggest that at 500 F and below the hot-salt problem is not particularly serious. It may be that service will later show that there are no failures at 500 F or less. In any case, a short-time failure would not be expected at this temperature from the evidence that is at hand. For skin stresses in tension at 550 F or above, the hot-salt problem should be of concern for the first supersonic transport. It may be desirable to use other metal for trim at points of highest temperature.

Since the mechanism of corrosion is not clearly established, it is rather difficult to predict what would happen in supersonic flight. There is some indication that movement of air decreases the susceptibility to hot-salt cracking. If this can be further established, certainly

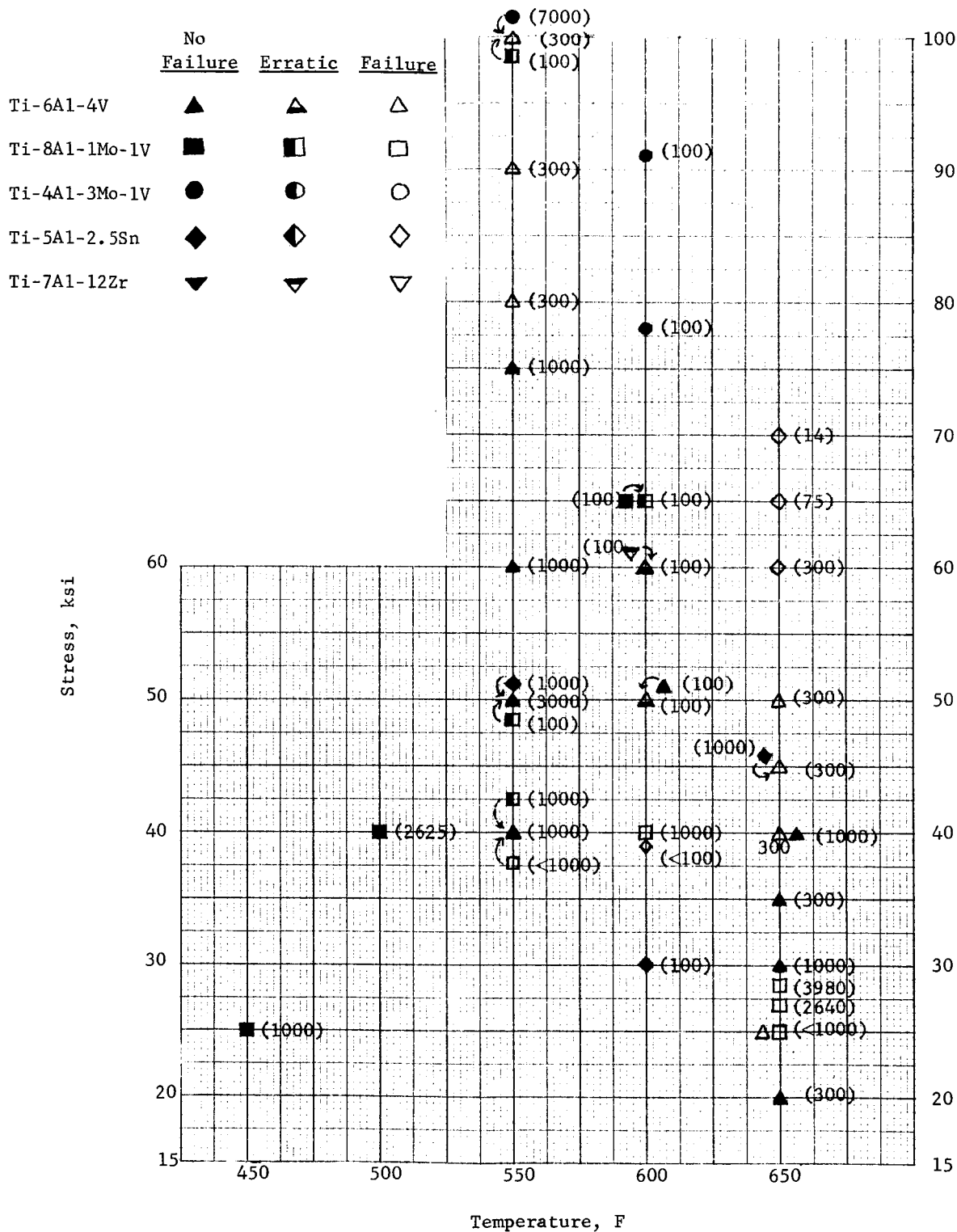


FIGURE 2. PLOT OF HOT-SALT STRESS-CORROSION CRACKING DATA FOR TITANIUM ALLOYS FROM VARIOUS LABORATORIES

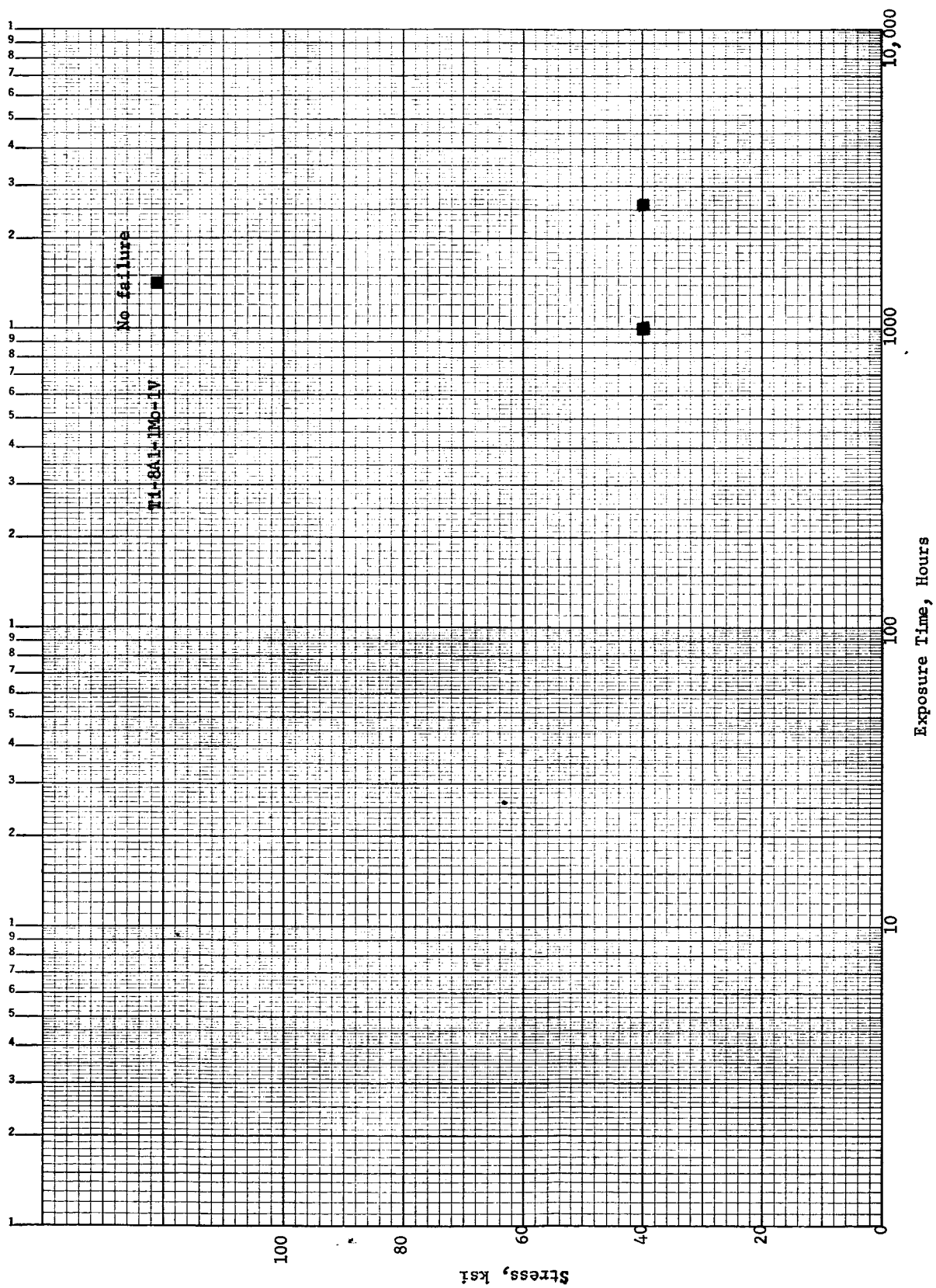
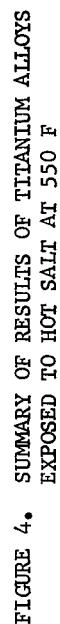


FIGURE 3. SUMMARY OF RESULTS OF TITANIUM ALLOYS EXPOSED TO HOT SALT AT 500 F



- x - Fractured in Exposure
 ● - Cracked in Exposure
 ○ - No Cracking Detected
 Prime' - Experimentally Processed Material
 c - Designates Crucible Data

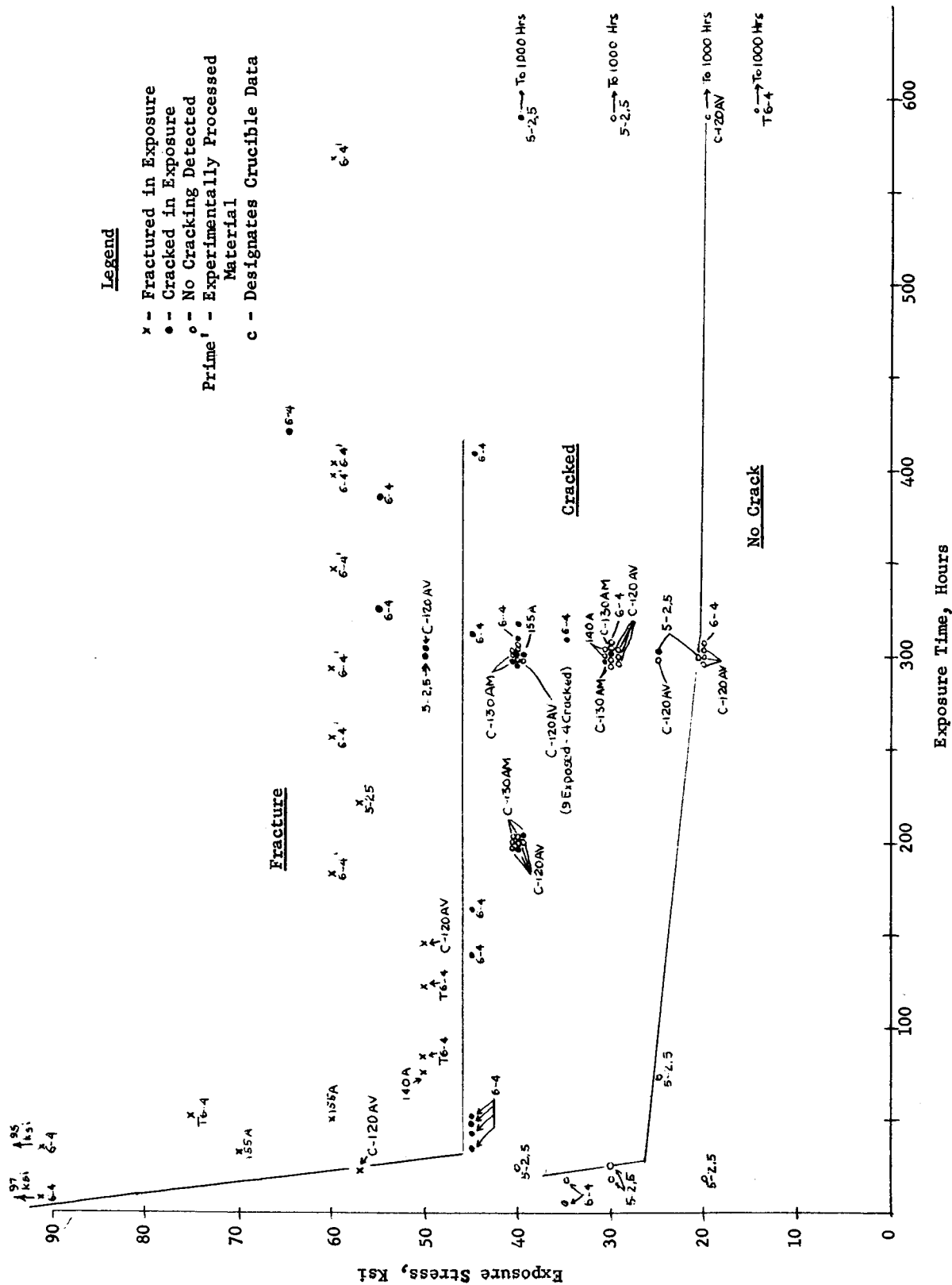


FIGURE 8. EXPOSURE STRESS VS. TIME FOR HOT SALT STRESS CORROSION AT 750 F

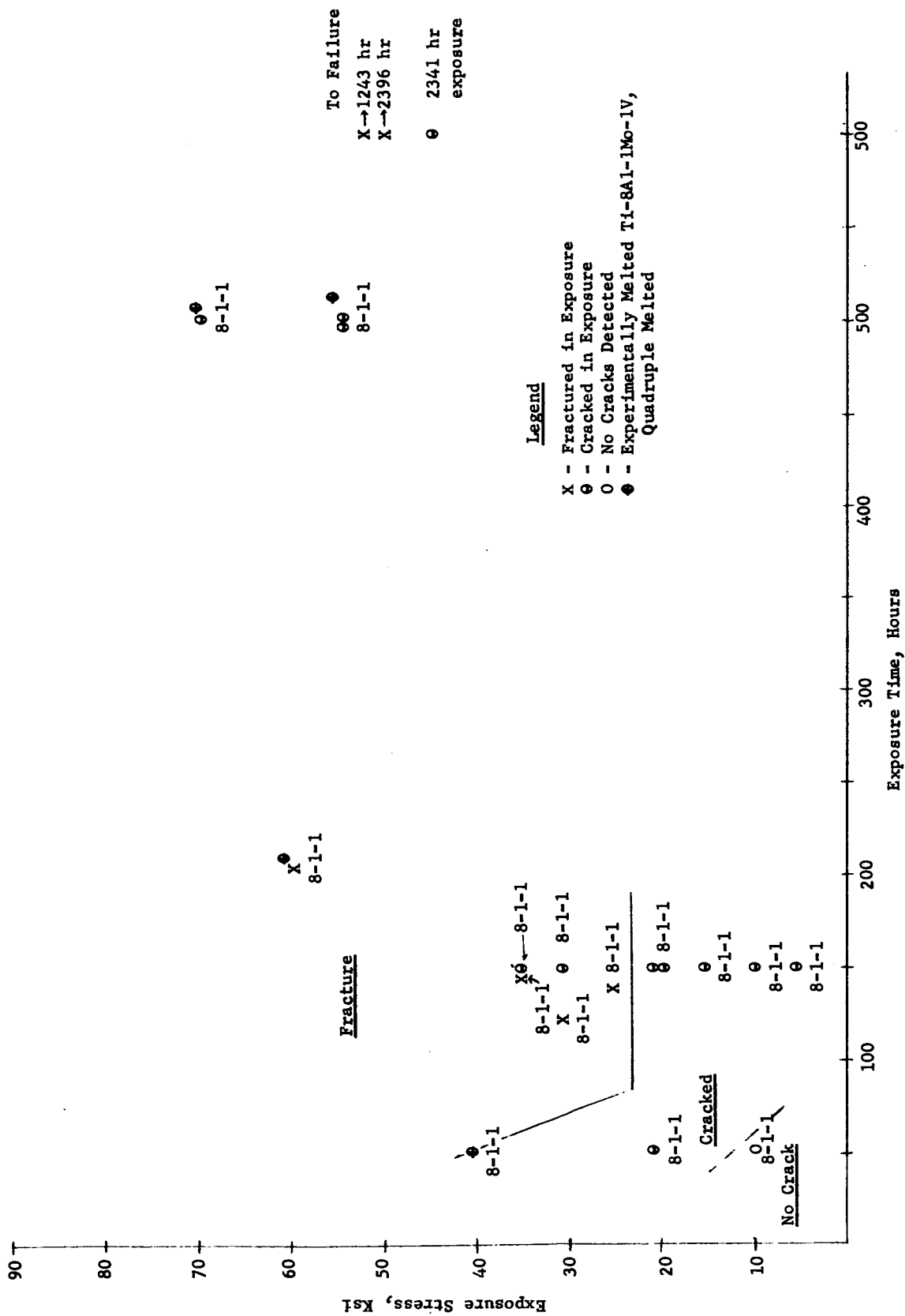


FIGURE 9. EXPOSURE STRESS VS. TIME FOR HOT SALT STRESS CORROSION AT 800 F

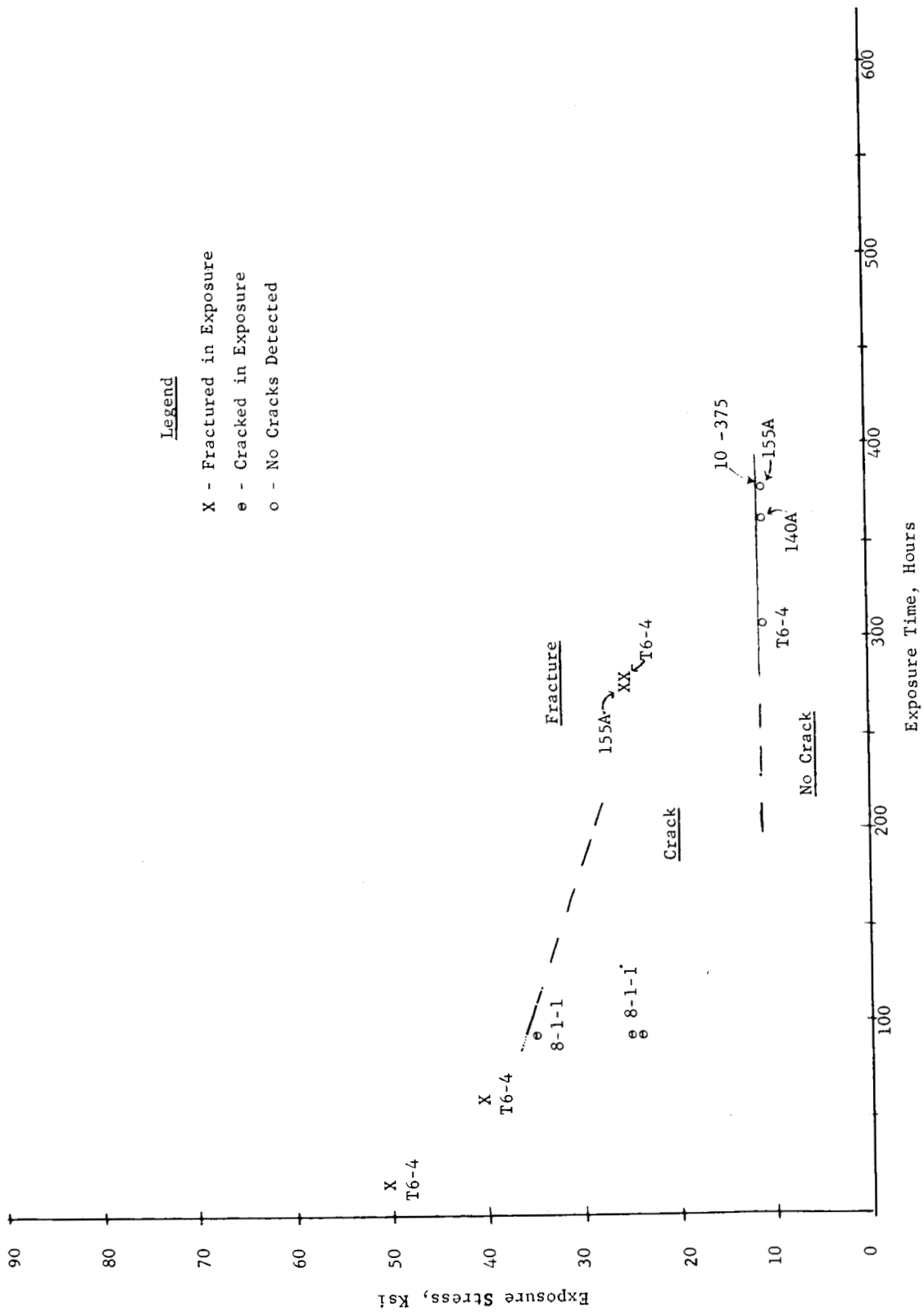


FIGURE 10. EXPOSURE STRESS VS. TIME FOR HOT SALT STRESS CORROSION AT 850 F

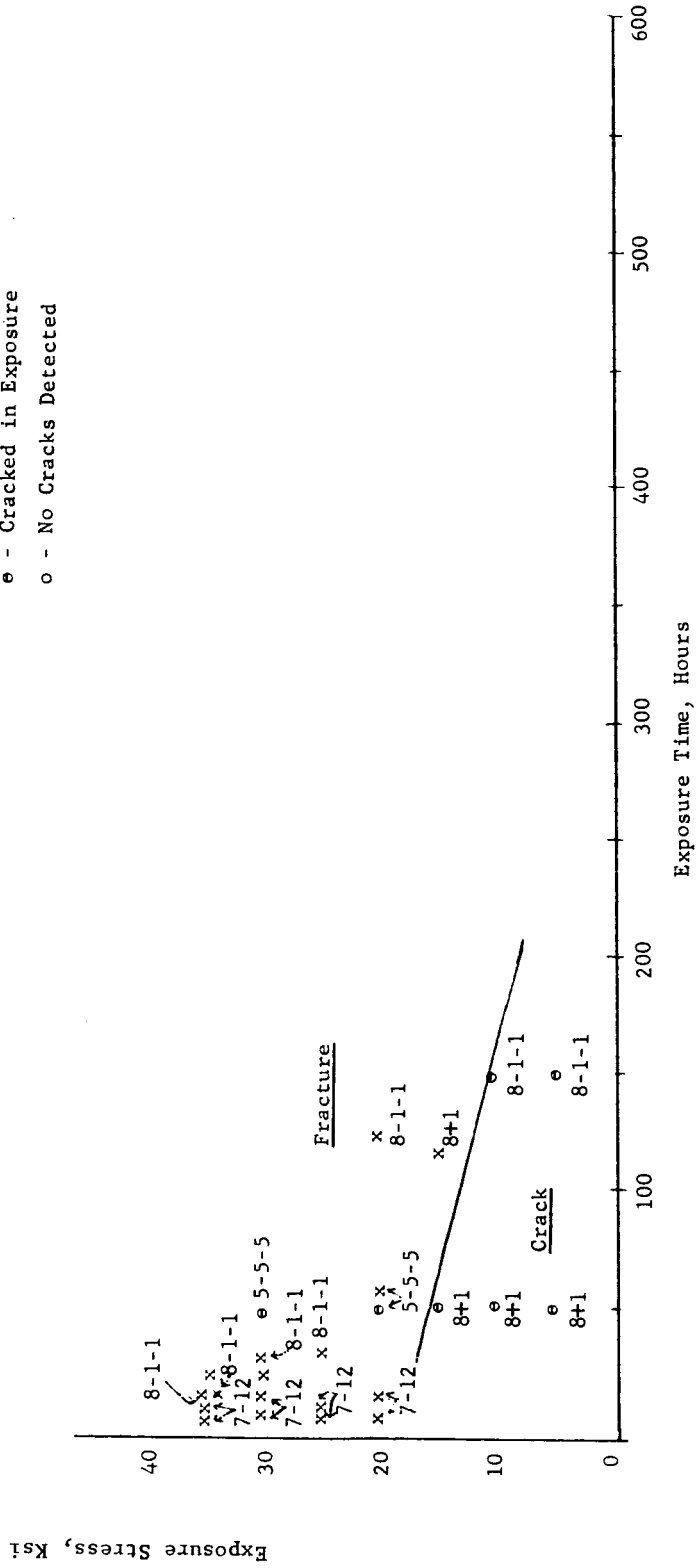


FIGURE 11. EXPOSURE STRESS VS. TIME FOR HOT SALT STRESS CORROSION AT 900 F

exposed parts then would not be expected to fail by this mechanism. However, in every aircraft structure there are crevices, lapped joints, and other structural configurations where salt can be trapped. Some of these areas have relatively stagnant conditions and cracks may originate in them. There is some evidence, however, that once the crack spreads out of a salt-contaminated area, the crack will stop. The crack-propagation susceptibility of the Ti-8Al-1Mo-1V alloy is being established and there is strong indication that titanium is not corroded in the vicinity of salt, but only when the alloy is in direct contact with salt.

In spite of the previously discussed data and the excellent service record of titanium, there is no sound method available at present for predicting whether a supersonic transport operating for 30,000 to 40,000 hours would experience hot-salt cracking. On the other hand, it should be remembered that many of the high-strength aluminum alloys, low alloy steels, and stainless steels are very susceptible to stress-corrosion cracking in marine environments even at ambient temperatures. In spite of this susceptibility, these alloys are extensively used in today's high-performance aircraft. Heat treatments, protective coating, and surface treatments have been developed through research. These minimize or completely eliminate the chance of premature failures due to stress-corrosion cracking.

Even if titanium alloys are found to be susceptible to hot-salt stress-corrosion cracking under operating conditions predicted for the SST, there is every reason to believe that through research, practical protective schemes can be developed to the same extent that they have been for other metals and alloys.

Until proved otherwise, titanium alloys should be considered as prime materials for the supersonic transport.

AREAS AND RECOMMENDATIONS FOR FUTURE WORK

This survey of the state of the art has brought out the fact that there is a scarcity of applicable data on the problem of the hot-

salt stress-corrosion cracking of titanium. The impression is that much of the work has been handicapped by programs too limited in scope and too restricted in support. Future research should be of both a fundamental and an applied nature. It should be coordinated through one central point so that the results of each program can be efficiently utilized to obtain in the shortest possible time answers to such questions as the following.

1. For a given alloy at a given temperature, what is the maximum tensile stress than can be employed on a salt-coated structural member for a life of 36,000 hours or more?
2. What is the maximum temperature for a given alloy below which no attack by hot salt is observed on tensile stressed samples close to the yield point?
3. What type and extent of preventive treatments, either during fabrication and construction, or during regular service maintenance, will minimize or prevent the occurrence of premature service failures.

Mechanism Studies

There is a prime need for a more extensive study of the mechanism of the hot-salt cracking. With a better knowledge of the mechanism of crack initiation and propagation, corrosion experiments simulating SST conditions could be planned more intelligently. The mechanisms proposed so far have been backed up by thermodynamic calculations, but there is certainly no general agreement on the kinetics of the reaction. It would seem that the most fruitful areas for basic research include:

1. Identification of the phases present in salt coatings after cracking has occurred, and identification of any gaseous phases given off as a result of heating titanium in the presence of salt.
2. A study of the role of moisture in the initiation and propagation of cracks.

3. A study of plastic versus elastic deformation in initiating cracking.
4. A study of the relationship of metallurgical factors such as fine structure, previous fabrication history, and grain size to cracking susceptibility. The use of transmission-electron microscopy should prove to be a useful tool in studying sub-grain structures in and around cracks.
5. Investigation of the nature of crack initiation from the electrochemical aspect. A study of the effect of applied potentials in promoting or inhibiting cracking, as well as a study of potentials existing between grain boundary phases and the body of grains would be expected to help elucidate the cracking mechanism and suggest means for preventing the attack.
6. It also would be of interest to determine whether or not cracking can be initiated by other halide salts, such as fluorides and bromides. In this connection the role of the anion in time to initiation of cracks might also be investigated.

Applied Studies

In a more practical manner, many of the factors known to exist in the environment should be included in the laboratory tests. It is suggested that the ASTM synthetic sea salt be used for all the laboratory evaluations instead of either pure sodium chloride or sea salt and that humidity be held at a constant level or at least recorded for each test.

Considerable expenditure has been involved in laboratory programs in which relatively short times of exposure were involved, such as a few hundred hours. Extremely long time tests of the order of 10,000 hours are needed to study the interrelation between temperature, stress, and salt. Also, there are a number of sites using temperatures considerably higher than the 400 to 500 F range of major interest to the

supersonic transport. At these higher temperatures in experimental programs, the time to failure is much shorter and failures are often observed in less than 100 hours.

In stress corrosion investigations time should be studied on a logarithmic scale in relation to stress or temperature. For example, if a sample with a particular combination of stress and temperature and hot salt fails in 1000 hours, lowering the severity of the exposure by decreasing either the stress or the temperature, or both, would only be considered an improvement if the time were extended another order of magnitude, namely, to 10,000 hours.

Many of the laboratory experiments with stressed samples only report time to failure. From the standpoint of the supersonic transport it is much more important to know (a) what time the first stress crack may be expected to appear, and (b) once it appears, how fast it will progress. The method employed at Langley Field recognized this problem. It may be possible to develop a creep test specimen in which the damage with time is followed continuously by the change in electrical resistance or by the change in the sonic response. A review of the available nondestructive measuring techniques for corrosion damage would be of assistance in setting up a system to continuously record loss of load carrying ability.

While stress, time, and temperature are all important, other parameters should also be included in the long-range study. For example, another factor is air velocity. Under Mach 3 conditions, the exposed surfaces of a plane would have large areas exposed to the violent sweeping of the air. This factor plus the flutter which occurs when the plane goes from subsonic to supersonic speeds may knock the salt off the surfaces. Some consideration should be given to simulating these factors in the laboratory.

In the higher atmosphere of around 75,000 feet the air becomes rarified. However, what air there is contains a higher percentage of ozone than is the case at ground level. Some studies should be made to establish that ozone is not more effective than oxygen in initiating cracking.

WKB/FWF:bcw
July 1, 1964

Acknowledgment

This state-of-the-art report reflects the views of a great many keen individuals who kindly cooperated in making information available. Some of these investigators have spent their careers specializing in this problem and their discussions were very helpful (see list in the Appendix).

Time unfortunately did not permit travel to a number of other laboratories. It is hoped that some of the people reading this report will be stimulated to prepare written discussions.

At Battelle Memorial Institute the authors are particularly indebted to their colleagues Dr. James J. Ward, James D. Jackson, and E. W. Cawthorne for ideas, information, and for reviewing the report. Staff members at the Defense Metals Information Center provided helpful current information on the supersonic transport from the Center.

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APPENDIX

List of Sites Visited and the Persons Contacted

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